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Molecular and Crystal Engineering of Polydiacetylenes:
Modification of Optical Properties

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1 Introduction

Polydiacetylenes have attracted a great deal of attention over the past decade due to their interesting electronic and optical properties [1,2]. It is also one of the few classes of polymeric materials that can be produced in the form of macroscopic single crystals [3]. These polymeric crystals are characterized by a tremendous richness of structure. A large number of side groups may be grafted onto the polymeric backbone stem which has a planar extended chain unsaturated structure (Fig. 1). The many different side groups (R and R') that can be part of the monomer structure have a strong influence on the crystalline organization and polymerization behavior in the solid state [4]. Depending upon the chemical nature of the side groups a number of crystalline phases may be present with different conformation of the side groups. Whether solid state polymerization in a particular crystalline phase will occur is dictated by the intermolecular spacings and precise arrangement of the adjacent diacetylene functionalities.

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The one dimensional nature of the unsaturated polydiacetylene backbone implies novel electronic and optical properties [5]. Large and fast third order optical nonlinearities were predicted for these materials and have subsequently been confirmed by a number of investigators [5]. These materials have been characterized by intense coloration, typically absorptive in the mid visible range with excellent transparency in the near infra-red. The absorption spectrum has essentially the same feature for most polydiacetylenes, viz., a sharp excitonic peak followed by the interband transition and they have been characterized as one dimensional semiconductors. However, the position of these features is very sensitive to the crystalline phase (organization of the side group). Significant thermochromic transition has been observed for a number of systems. It is believed that side group induced "stresses" in the backbone effecting its geometry, planarity and conformation in general, is responsible for the change in its electronic structure resulting in such thermochromic shifts. Solvatochromism also has been studied for soluble polydiacetylenes. Again, the extent and nature of solvation of the side groups indirectly influences the backbone geometry effecting its electronic structure [6].

The extended polydiacetylene backbone whether it is in a solution, a single crystal or a monolayer is

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confined in this geometry by the arrangement of the side groups. Its electronic structure is a sensitive function of this geometry. This is dramatically demonstrated in the case of substituted polyacetylenes. The extended chain geometry in polyacetylene is easily distorted as bulky side groups are substituted. This is reflected in the dramatic change of the electronic properties, and a ten orders of magnitude drop in the level conductivity is seen upon doping [7].

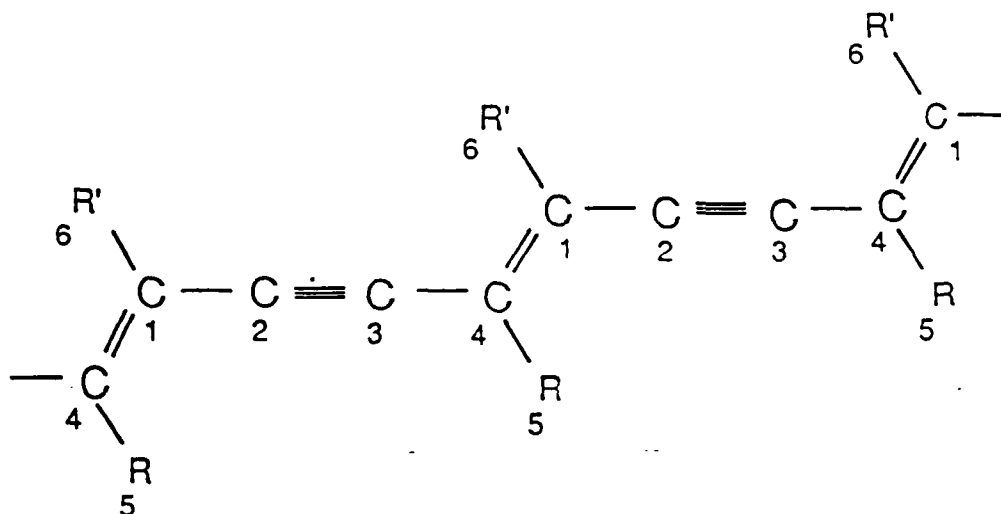


Fig. 1. Structure of the polydiacetylene backbone. The numbers label the carbon atoms on the backbone and the single masses representing the sidegroups R and R'

ORCHARD and TRIPATHY [6] in a recent publication investigated the influence of the coupling of the side group electronic structure to that of the backbone, in polydiacetylenes. The anticipated changes in the absorption spectrum when the saturated alkyl side groups are replaced with phenyl groups coplanar with the backbone are spectacular. The rhetorical question one asks, if the side groups as the mechanical tuners are replaced by electronic tuners, how will the backbone properties be modulated? The side groups may be a photochromic group or bridged donor-acceptor moiety, for example. Of course any such "molecular engineering" will necessarily have to be tempered with "crystal engineering". The backbone extended chain geometry should be maintained and side groups must find themselves in such a packing as to produce the maximum interaction. In the present paper, the crystal and molecular engineering aspects of a class of polydiacetylenes synthesized and processed with the above goal is discussed.

2 Methods

Symmetric diacetylene monomer with the substituents 4-n-Butyl, 2,3,5,6,-tetrafluoro phenyl (BTFFP) was synthesized according to the method of Okuhara et al. [8]. The method of synthesis and purification procedures are listed elsewhere. This monomer is melt stable and polymerization in the

monomer crystal may be carried out using UV radiation. Thin film single crystals were prepared between two quartz plates from both melt and solution. The crystal growth technique developed by THAKUR and coworkers was used in this process [9]. Polymerization in the thin film single crystal results in a deep blue film. Visible spectra from thin polymerized films were obtained.

The electronic structure of an analog of this polydiacetylene was calculated following the methods outlined by ORCHARD and TRIPATHY [6]. Full free valence geometry optimized structures of bis-phenyl diacetylenes were used in conjunction with the Valence Effective Hamiltonian technique [10] for the band structure calculation. These calculations were performed as a function of bond rotation about the bond linking the phenyl group to the polydiacetylene backbone. The torsion angles have been determined for BTFP from x-ray diffraction studies. Band gap for this geometry is compared with the spectral features seen for the thin film single crystals.

3 Results and Discussion

Short chain oligomers of poly bis-phenyl diacetylenes were used to obtain the optimized geometries. The total molecular energies were calculated for increasingly larger oligomers using the MNDO option in the chemical software package Chemlab-II (Molecular Design, Ltd.). As the size of the oligomer increases, the corresponding energies per repeat unit reach an asymptotic value. While the ends of the chain perturb the geometries of the penultimate units, once the energy/repeat unit has reached the asymptotic value geometries of the central unit may be used to construct the polymer for the calculation of the electronic band structure.

The MNDO optimized geometries for hydrogen and phenyl substituted polymers are listed in Table 1. For the symmetric diacetylene considered, two phenyl rings per repeat unit were used to determine the spatial dependence of the inductive effect along the polymer backbone. The electronic band structure was calculated using the Valence Effective Hamiltonian method developed by NICHOLAS and DURAND [10]. A portion of the electronic band diagram for phenyl substituted polydiacetylene is given in Fig. 2, when the phenyl group is coplanar with the polydiacetylene backbone. Figure 3 compares this with the band structure of hydrogen substituted polydiacetylene.

Table 1. Optimized bond lengths and bond angles for polydiacetylenes with R=R'=H and R=R'=phenyl

		H	Phenyl	DTIC TAB	Unannounced	Justification
Bond Length [Å]	d2-3	1.2024	1.2041		<input checked="" type="checkbox"/>	
	d3-4	1.4140	1.4159		<input type="checkbox"/>	
	d4-1	1.3579	1.3989		<input type="checkbox"/>	
Bond Angle [°]	∠3-4-1	123.9	123.9			
	∠3-4-5	115.3	115.3			

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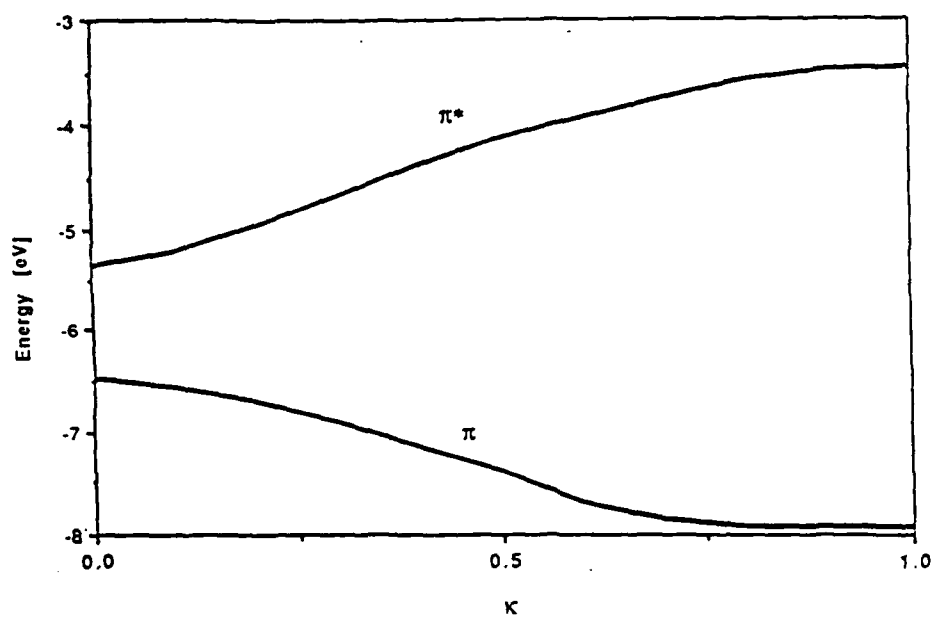


Fig. 2. VEH band structure for phenyl-disubstituted polydiacetylene showing band gap for π - π^* transition ($\kappa=\pi/a$)

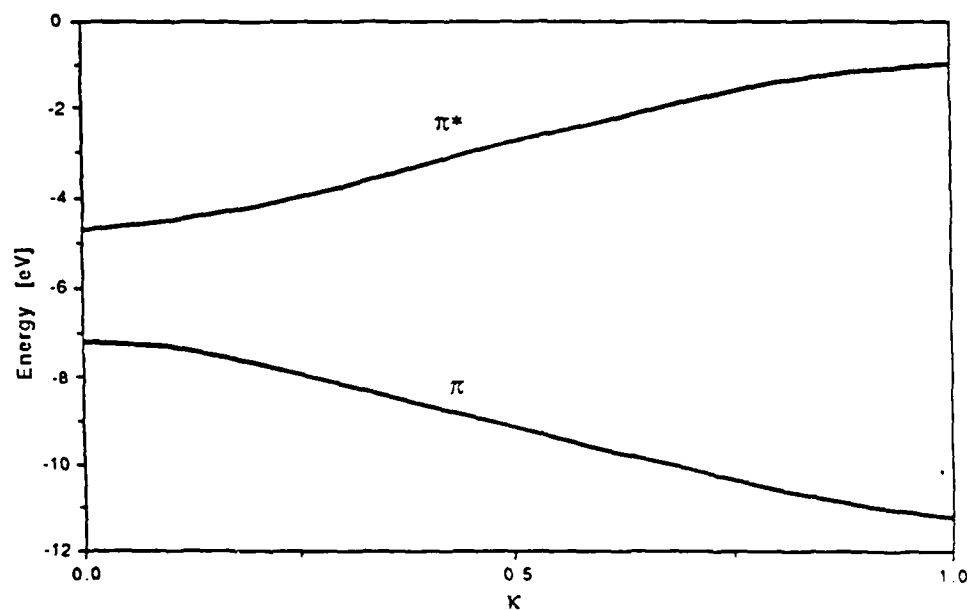


Fig. 3. VEH band structure for polydiacetylene showing band gap for π - π^* transition ($\kappa=\pi/a$)

There is a significant narrowing of the gap as a result of the inductive effect from the coplanar phenyl side group. However, it is rarely possible that such idealized geometries will be realized in a real crystal. The substituent group may adopt one of a large number of conformations accessible to it, in order that a minimum in the packing energy is obtained. One may attempt to lock the side group in a specific conformation by appropriate substitution of the phenyl rings and this was the motive in selecting BTFP, yet the results are not straight forward. Crystal structure determination from bulk grown crystals of BTFP indicate the phenyl ring to be at 58° angle to the polydiacetylene plane.

The electronic structure calculations were repeated, with the phenyl ring incrementally rotated out of the plane of the polydiacetylene backbone. In Fig. 4 the band gap which is directly given by the position of the optical transition is plotted as a function of the torsional angle made by the phenyl ring with the plane of the polydiacetylene backbone. At 90° angle we see the band gap increasing toward the gap of a hydrogen substituted polydiacetylene. The π conjugation from the side group to the backbone has been lost. At 58° angle this conjugation has already significantly dropped off and the optical absorption is not expected to be very dissimilar from other known diacetylenes. At 30° the band gap appears to go through a minimum. The shift of the minimum in the band gap from 0° to 30° may be the result of the decrease in the strain in the backbone as the steric hindrance between the adjacent phenyl groups is decreased.

Figure 5 is a visible absorption spectrum taken from a thin single crystal of the polydiacetylene BTFP. The spectrum is indicative of a two phase system. MATSUDA and coworkers [11] have identified one of the crystal phases of this polydiacetylene and have carried out the detailed crystal structure. X-ray diffraction studies from the thin film single crystal will have to be carried out to identify the correct phase in these thin single crystals.

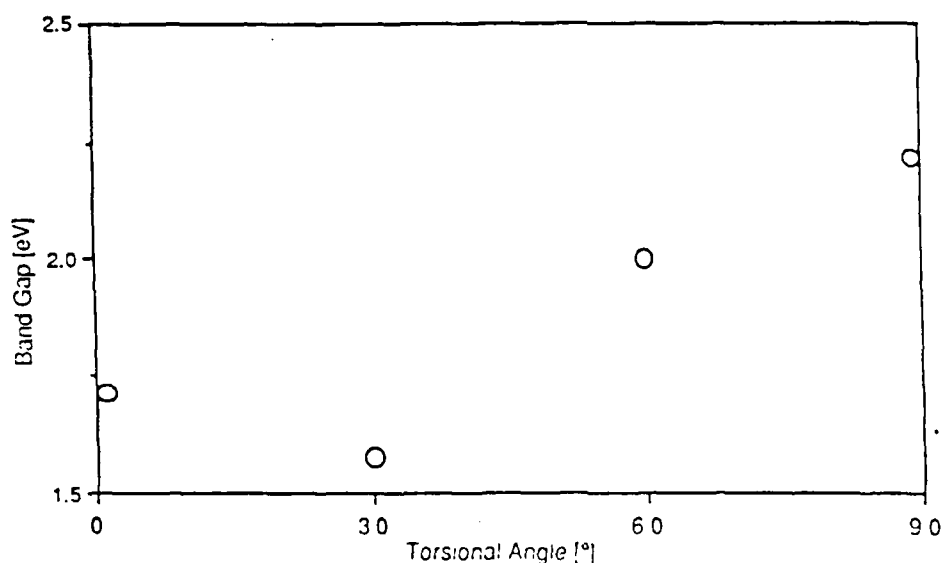


Fig. 4. Band gap of phenyl disubstituted polydiacetylene with rotation of phenyl groups. 0° indicates the phenyl rings are planar with the backbone

The theoretical calculations carried out on the model system are in excellent agreement with the experimental results. We believe our efforts at molecular engineering of the diacetylene system to possess electroactive side groups is appropriate. However, better ground rules for crystal engineering has to be established in order that optimal conjugation of the side group and backbone electronic structure may occur.

Figure 5 indicates that if the torsion angle of the phenyl ring could be reduced to about 25° a significant red shifting of the absorption edge will occur. This is the direction our present crystal and molecular engineering effort is taking. A number of approaches can be postulated where the electroactive side groups may be coaxed into a coplanar arrangement. This may be achieved, for example, through hydrogen bonding. Appropriately modified side groups to contain donors and acceptors to form a charge transfer bridge may be another approach. Side groups adjacent to each other may be modified to undergo dimerization in the solid state. This may be brought about simultaneously with the solid state polymerization through the diacetylene or in a two-step process [12].

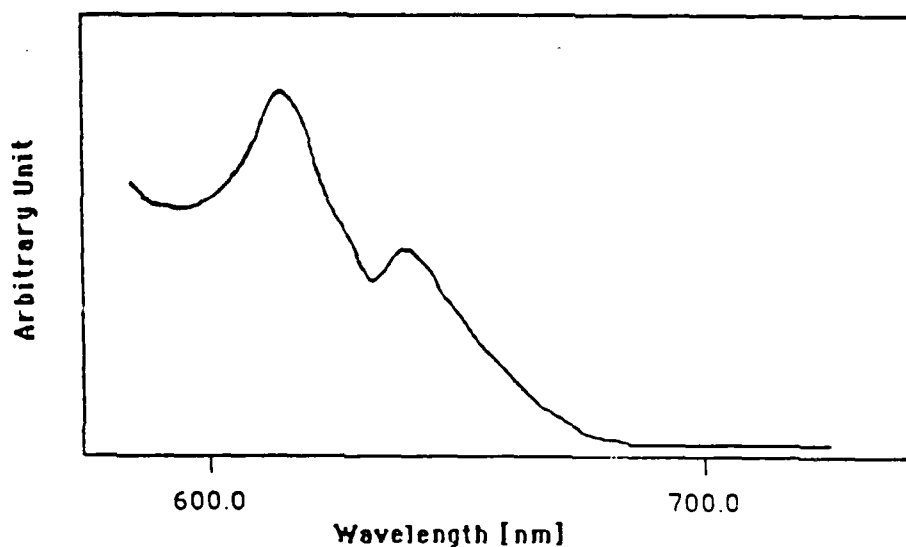


Fig. 5. Visible absorption spectrum for BTFP

The nonlinear optical properties are expected to be very sensitive to the position of the optical gap. In addition these properties may be modulated through side group induced processes. Asymmetrically substituted surfactive diacetylenes suitable for monolayer growth may provide a more convenient vehicle for the molecular and crystal engineering concepts discussed here. This is expected to play a significant role in our continuing efforts in this area.